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TECHNICAL REPORT

WSRL-0563-TR

SYNTHESES AND CHARACTERISATIONS OF DERIVATIVES OF ETHYL CENTRALITE

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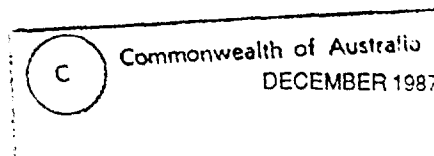
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SYNTHESES AND CHARACTERISATIONS OF DERIVATIVES OF ETHYL CENTRALITE

N.J. Curtis

S U M M A R Y

A comprehensive description is given of the preparations of all the major derivatives of ethyl Centralite that are found in nitrocellulose based propellants. These compounds are fully characterised by spectroscopic and thin-layer techniques.



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1. INTRODUCTION

Ethyl Centralite is a commonly used stabiliser for single, double and triple base propellants (Table 1). Upon reaction with the oxides of nitrogen formed when propellant deteriorates, ethyl Centralite is converted to a variety of nitro urea, aniline and nitrosamine derivatives(ref.1). Scheme 1 shows the proposed paths to the derivatives of ethyl Centralite that have been demonstrated or postulated to be present in degraded propellant(ref.1,2,3,4).

The purpose of this report is to give a comprehensive description of the preparations of these derivatives of ethyl Centralites, and provides full characterisation by nuclear magnetic resonance spectroscopy, infra-red spectroscopy, ultra-violet/visible spectroscopy and thin layer chromatography. The report serves to complement similar work associated with the use of diphenylamine(ref.5,6) as a stabiliser.

2. PREPARATIONS OF DERIVATIVES OF ETHYL CENTRALITE

The best and most general method available for the preparation of the nitro urea derivatives was via the N-alkylation of the mono- and dihydrido nitro derivatives of 1,3-diaryl ureas. These precursors were readily prepared by coupling of the appropriate nitroaniline and nitrophenylisocyanate. Good yields were readily obtained for 2-nitro ethyl Centralite, 4-nitro ethyl Centralite, 2,2'-dinitro ethyl Centralite and 2,4'-dinitro ethyl Centralite. Whilst 4,4'-dinitro ethyl Centralite may also be prepared using this procedure, nitration of ethyl Centralite itself proved to be easier experimentally.

The unnitrosated N-ethylaniline derivatives were best prepared by condensation of ethylamine with the appropriate halonitrobenzene in dimethylformamide solution, at room temperature. The reactions do not proceed when run in ethanol solution and this is a consequence of the lower polarity of the medium(ref.5). An aqueous solution (70%, w/w) of ethylamine may be used satisfactorily in place of the pure liquid.

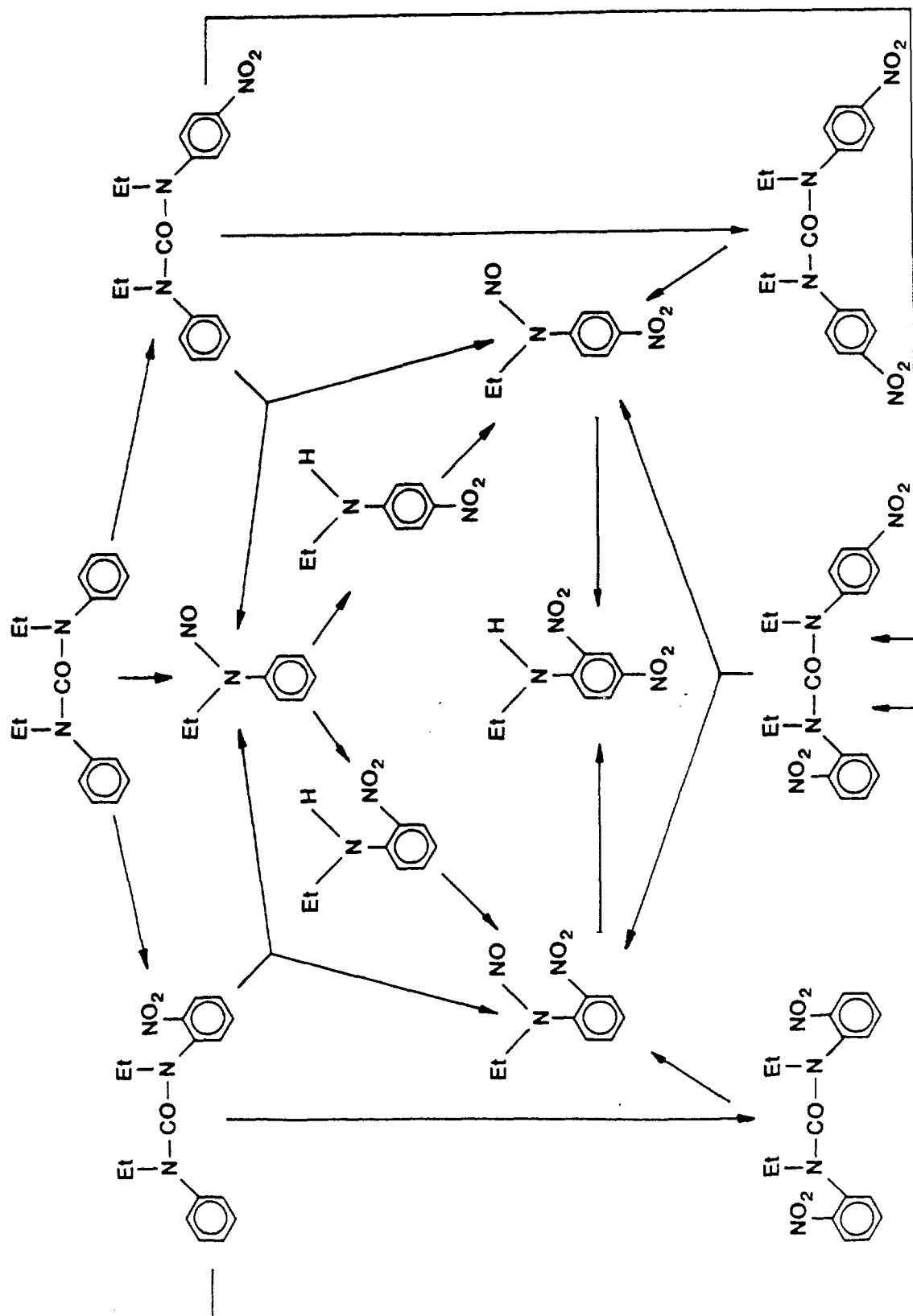
N-Nitrosated N-ethylaniline derivatives were readily prepared by the action of sodium nitrite on an acetic acid solution of the appropriate N-ethylaniline. The interrelations of these three classes of derivatives of ethyl Centralite are shown in Scheme 1.



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Scheme 1

FORMATION OF ETHYL CENTRALITE DERIVATIVES IN PROPELLANTS



3. EXPERIMENTAL PROCEDURES

3.1 2- and 4-nitrobenzazide

Whilst both 2- and 4-nitrophenylisocyanate are available commercially they are moisture sensitive and old samples frequently contain the corresponding dinitro ureas. Alternatively the benzazide may be used which can be rearranged in situ (the Curtius rearrangement) to give the desired starting material(ref.7). These benzazides are readily prepared from the nitroaromatic acid via the aroyl chloride and are much less water sensitive than the isocyanate. The procedures for the two isomers were similar and are exemplified by the preparation of 2-nitrobenzazide.

To a solution of 16.7 g (0.10 mol) of 2-nitrobenzoic acid in a mixture of 100 mL chloroform and 1 mL dimethylformamide was added 10.9 mL (0.15 mol) of thionyl chloride and the mixture refluxed for 1 hour. The resultant clear solution was evaporated under reduced pressure to give an oil such that the temperature was kept below 30°C (to avoid discolouring). This oil was dissolved in 30 mL acetone and added over 10 min to a solution of 7.8 g (0.12 mol) sodium azide in 50 mL water. The reaction mixture was kept in the range 15 to 20°C during the addition and once this was completed, the cooling bath was removed and the reaction mixture stirred for a further hour. An oil separated out. Water (50 mL) was then added, the mixture placed in the freezer, the resultant solid filtered, washed well with water and dried in air. The crude product was dissolved in toluene (40 mL) at 40°C, decolourised with charcoal and 80 mL 40-60 petroleum ether added. An oil was initially formed but this solidified to a mass of pale yellow needles. Yield was 13.55 g (71%) with melting point 38-9°C. Lit 39°C(ref.8).

4-Nitrobenzazide was prepared in a similar manner, except that the crude product precipitated from the reaction mixture on addition to the azide solution but was collected as before. Recrystallisation was effected by dissolution in 60 mL toluene at 40°C and addition of 60 mL petroleum ether to the decolourised solution. Near white needles appeared on cooling. Yield was 12.80 g (67%) with melting point 70-1°C. Lit 71-2°C(ref.9).

Conversions to the isocyanates were achieved by heating in toluene (25 mL/0.01 mol) under reflux for 30 min. Molecular nitrogen was formed during the rearrangement and the use of a bubbler indicates the start and end of the reaction. The reaction mixtures were then allowed to cool before treatment with aniline. The procedures below (Sections 6.2 to 6.5) refer to isocyanate either derived from the benzazide in situ or from a fresh sample. All these reactions were carried out in the presence of a crystal of toluene-4-sulphonic acid and under nitrogen.

3.2 2-Nitro ethyl Centralite via 1-ethyl-3-(2-nitrophenyl)-1-phenylurea

N-ethylaniline (2.77 mL, 0.022 mol) was added to 0.02 mol 2-nitrophenylisocyanate (ex 3.84 g 2-nitrobenzazide) in 50 mL toluene and the mixture refluxed for 30 min. The cooled reaction mixture was evaporated under reduced pressure to produce an oil which could be induced to solidify by the addition of ethanol and re-evaporation. The product was dissolved in 20 mL boiling ethanol, 20 mL 60-80 petroleum ether added to the hot solution and left to cool. Yellow needles of 1-ethyl-3-(2-nitrophenyl)-1-phenylurea were obtained with melting point 90-1°C(ref.7). Yield was 4.68 g (82%).

To a solution of 1.43 g (0.005 mol) of the above urea in 20 mL dry dimethylformamide, under nitrogen, was added 0.31 g of 46% sodium hydride (0.006 mol). An intense red colour resulted and the mixture was stirred

for a few minutes and then 1.0 mL iodoethane (ca 0.0125 mol) was added. Upon very gentle heating (iodoethane boils at ca 60°C) the colour slowly faded and after 30 min had mostly gone. The reaction mixture was put on a rotary evaporator after a further 30 min (to remove excess iodoethane) and then added to 200 mL water. This was extracted with dichloromethane (3 x 200 mL), the organic solutions combined and dried, and subsequently evaporated to an oil which could not be induced to crystallise. Thin layer analysis indicated two major components: the required compound showed a UV active spot which had a smaller R_f than a yellow impurity. The oil was loaded onto a silica column (200 x 25 mm) in a small volume of 60-80 petroleum ether and eluted with 10% ethyl acetate in petroleum ether. The appropriate fractions were combined, evaporated and recrystallised from 20 mL 60-80 petroleum ether to give 0.98 g (62%) of pale yellow needles with melting point 55-7°C. Lit 56-7°C(ref.10).

3.3 4-Nitro ethyl Centralite via 1-ethyl-3-(4-nitrophenyl)-1-phenylurea

N-Ethylaniline (5.54 mL, 0.044 mol) was added to 0.04 mol 4-nitrophenyl-isocyanate (ex 7.68 g 4-nitrobenzazide) in 100 mL toluene, the mixture refluxed for 30 min, cooled and evaporated under reduced pressure to give an oil. This was dissolved in 50 mL of ethanol at room temperature and precipitated by the addition of 100 mL of 60-80 petroleum ether. The white product was recrystallised from a boiling 4:1 mixture of 60-80 petroleum ether and ethanol respectively. Yield of white needles 9.82 g (86%) with melting point 47-9°C. The urea obtained in this case was metastable and slow conversion to a higher melting form (79-80°C) was observed over a period of months (see ref.7).

The crude product was obtained in an analogous manner to that described for 2-nitro ethyl Centralite. Thin layer analysis showed the reaction mixture to contain only one spot (by UV). The oil was dissolved in a small volume of 60-80 petroleum ether containing a few drops of ethyl acetate for dissolution and loaded onto a silica column (200 x 25 mm). Elution with 10% and then 20% ethyl acetate in petroleum ether gave the product in pure form after evaporation of the relevant fractions. The oil was treated with petroleum ether followed by evaporation under reduced pressure thrice (to remove traces of ethyl acetate) and then left under 20 mL petroleum ether in a freezer overnight. Scratching of the cold mixture effected slow crystallisation as a very pale yellow solid. The yield was 1.04 g (66%) with melting point 42-5°C (see ref.1,7). An unstable complex is said to be formed with ethanol(ref.10) and this solvent should be avoided.

3.4 2,2'-Dinitro ethyl Centralite via 1,3-bis(2-nitrophenyl)urea

2-Nitroaniline (6.08 g, 0.044 mol) was added to 0.04 mol 2-nitrophenyl-isocyanate (ex 7.68 g 2-nitrobenzazide) in 100 mL toluene, the mixture refluxed for 2 hours, and left to cool. A precipitate was formed on cooling and this was collected. The filtrate was reduced in volume, under reduced pressure, to 25 mL and a second crop obtained. The combined precipitates were recrystallised by dissolving in 100 mL boiling acetone/40 mL dimethylformamide. The hot solution was filtered and left to cool. A 55% yield (6.65 g) of pale yellow needles was obtained with melting point 233-4°C(ref.7). Lit 225°C(ref.11).

To a solution of 1.51 g (0.005 mol) of the above urea in 20 mL dry dimethylformamide, under nitrogen, was added 0.63 g of 46% sodium hydride (0.012 mol) to give a deep red mixture. This was treated with 2.0 mL (ca 0.025 mol) of iodoethane as before. After 1 hour of very gentle heating, excess iodoethane was removed on a rotary evaporator and the reaction mixture added to 500 mL water. The crude product precipitated out and was filtered off and well dried. Three recrystallisations from 10 mL

of boiling ethanol gave the product as conglomerated yellow needles with melting point 142-3°C(ref.7). The yield was 1.12 g (63%).

3.5 2,4'-Dinitro ethyl Centralite via 1-(2-nitrophenyl)-3-(4-nitrophenyl) urea

4-Nitroaniline (4.50 g, 0.033 mol) was added to 0.03 mol 2-nitrophenyl-isocyanate (ex 5.76 g 2-nitrobenzazide) in 75 mL toluene and the mixture refluxed for 2 hours. The product crystallised as orange needles quickly in the hot reaction mixture and this was completed by cooling. The product was filtered and was satisfactory for use without further purification. The yield was 7.73 g (85%) and the compound melted at 258°C, apparently with decomposition, solidified and remelted at 277-8°C(ref.7). Lit 270-5°C sub(ref.8).

Although in this case the starting urea was not completely dissolved, the analogous reaction conditions for the preparation of 2,2'-dinitro ethyl Centralite were used successfully. The crude product precipitated as before and was recrystallised twice from 75 mL of 2:1 60-80 petroleum ether/ethanol to give 0.99 g (55%) of the product as yellow flakes with melting point 138-9°C(ref.7).

3.6 4,4'-Dinitro ethyl Centralite via ethyl Centralite

To a solution of 20 mL concentrated nitric acid in 80 mL glacial acetic acid was added 10.0 g (0.037 mol) ethyl Centralite over 5 min. The addition caused the temperature of the solution to rise to ca 50°C and the solution turned orange. After leaving to cool for one hour, the reaction mixture was added to 500 g ice-water with rapid stirring and subsequently extracted with dichloromethane (2 x 200 mL). The combined organic layers were washed with water, aqueous potassium carbonate, water and then dried and evaporated. The resultant oil was dissolved in 200 mL boiling ethanol, decolourised and evaporated to a solid. Thin layer analysis indicated that the major products isolated were 2,4'-and 4,4'-dinitro ethyl Centralite. Two recrystallisations from 150 mL methanol gave large, very pale yellow plates of the considerably less soluble 4,4'-dinitro ethyl Centralite with melting point 147-8°C. Lit 147°C(ref.1). The yield was 6.45 g (48%).

3.7 N-Ethyl-2-nitroaniline

To 7.05 g (0.05 mol) of 2-fluoronitrobenzene dissolved in 50 mL dimethyl-formamide was added 16.4 mL (0.25 mol) of ethylamine over a period of 5 min. An exothermic reaction occurred and the mixture rapidly turned orange. After 15 min the reaction mixture was added to 250 mL water and extracted with dichloromethane (2 x 200 mL). The combined organic layers were washed with water (3 x 200 mL), dried and evaporated to an oil. The oil was then fractionally distilled and the orange material boiling at 100°C (0.7 Torr) was collected. The resultant oil solidified in the refrigerator but was a liquid at room temperature(ref.1). Aqueous ethylamine may be used effectively in this preparation, instead of the neat liquid.

3.8 N-Ethyl-4-nitroaniline

To 7.05 g (0.05 mol) of 4-fluoronitrobenzene dissolved in 50 mL dimethyl-formamide was added 16.4 mL (0.25 mol) ethylamine. The reaction was less vigorous than with the 2-isomer and slowly turned yellow. After 2 hours stirring, the reaction mixture was poured into 500 mL water and the resultant yellow precipitate filtered. This was recrystallised from 30 mL boiling 1:1 ethanol/water to give 7.92 g (95%) of yellow needles with melting point 94-5°C. Lit 95-96°C(ref.1). Aqueous ethylamine may be used effectively in this preparation, instead of the neat liquid.

3.9 2,4-Dinitro-N-ethylaniline

To 10.13 g (0.05 mol) of chloro-2,4-dinitrobenzene in 50 mL dimethylformamide was added 16.4 mL (0.25 mol) ethylamine over 2 min. The reaction was rapid and exothermic, and after 10 min the reaction mixture was added to 500 mL water. The resultant precipitate was recrystallised from 120 mL boiling ethanol to give orange plates with melting point 114-5°C. Lit 113.7-114.5°C(ref.1). The yield was 9.73 g (92%). Aqueous ethylamine may be used effectively in this preparation, instead of the neat liquid.

3.10 N-Ethyl-N-nitrosoaniline

To 6.06 g (0.05 mol) of N-ethylaniline dissolved in 50 mL glacial acetic was added a solution of sodium nitrite (6.9 g, 0.1 mol) in 10 mL water, over 5 min. After 15 min stirring, 100 mL water was added and the mixture extracted with dichloromethane (2 x 50 mL). The combined organic layers were washed with water (2 x 100 mL), aqueous potassium carbonate, dried and evaporated to an oil. The residue was distilled from a preheated oil bath (120°C) to give 5.21 g (69%) of the product as a pale yellow oil with boiling point 60°C (0.4 Torr). Lit 150-4°C at 41 Torr(ref.1).

3.11 N-Ethyl-2-nitro-N-nitrosoaniline

To 1.66 g (0.01 mol) of N-ethyl-2-nitroaniline dissolved in 20 mL glacial acetic acid at room temperature was added a solution of 3.45 g (0.05 mol) sodium nitrite in 5 mL water over 2 min. A colour change from orange to yellow resulted. After 10 min stirring, 50 mL water was added and the mixture placed in the refrigerator. An oil appeared which solidified with time and which was then filtered. The solid was then dissolved in 10 mL of ethanol, at room temperature, and 20 mL of 60-80 petroleum ether slowly added. Very pale yellow needles (1.56 g, 80%) were obtained after cooling in a refrigerator and these had melting point 32-4°C. There is no recorded melting point in the literature, however the UV spectrum was similar to that published(ref.12).

3.12 N-Ethyl-4-nitro-N-nitrosoaniline

To 1.66 g (0.01 mol) of N-ethyl-4-nitroaniline dissolved in 40 mL glacial acetic acid at room temperature was added a solution of 3.45 g (0.05 mol) sodium nitrite in 5 mL water over 2 min. Yellow plates appeared on stirring and after 15 min, 100 mL water was added. The cooled mixture was filtered, well washed with water and then air-dried. Recrystallisation from 20 mL boiling ethanol gave flat yellow plates with melting point 119-120°C. Lit 120.7-121.2°C(ref.1). The yield was 1.84 g (94%).

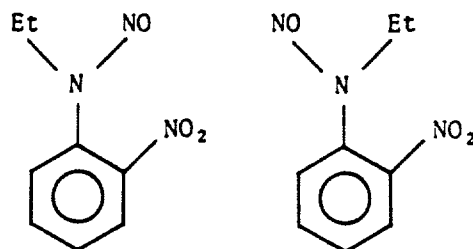
4. SPECTROSCOPIC CHARACTERISATION

4.1 Proton nuclear magnetic resonance spectra

Proton nmr spectra were recorded in d_6 dimethylsulphoxide solution using a Bruker WP-80 instrument. Chemical shifts (Table 2) are downfield from internal tetramethylsilane. Integrations and multiplicities were in accord with expected results.

Two sets of signals for the ethyl protons are seen for N-ethyl-2-nitro-N-nitrosoaniline and are a consequence of the restricted rotation about the aromatic carbon-amine nitrogen bond which effects two configurations (Scheme 2).

Scheme 2



This behaviour was not seen for the less hindered *N*-ethyl-4-nitrosoaniline.

4.2 Infra-red spectra

Fourier-transform infra-red spectra were run on melt or thin film (dichloromethane cast) samples using a Perkin-Elmer 1750 model. They are collectively shown in figure 1. All urea compounds show prominent absorption in the range 1640 to 1670 cm^{-1} associated with carbonyl stretching. In addition, peaks are observed at 1520 - 1530 cm^{-1} and 1340 - 1350 cm^{-1} which are consistent with asymmetric and symmetric stretches, respectively, of the nitro group. These are more intense for the dinitro compounds. The anilinic compounds all show a sharp single peak at 3360 - 3400 cm^{-1} consistent with a secondary amine and due to N-H stretching, and these absorptions are absent in the nitrosamines. Apart from these absorptions, the spectra are difficult to interpret and are best used for "fingerprint" comparisons.

4.3 Ultra-violet/visible spectra

Electronic spectra were recorded in ethanol solution (ca 10^{-4} M) using a Perkin-Elmer Lambda 5 instrument and are shown collectively in figure 2. Absorption maxima and extinction coefficients (ϵ in units of $\text{mol dm}^{-3}\text{cm}^{-1}$) are shown in Table 3 along with literature values (ref.3,12). In general, the agreements are very good.

The chromophores due to the unsubstituted and 2-nitro-*N*-ethylphenyl groups in the ureas are similar with maxima at ca 245 nm . In contrast, ureas containing the equivalent 4-nitro group show absorption maxima at longer wavelengths of ca 320 to 330 nm . In addition, both 2-nitro and 2,2'-dinitro ethyl Centralite exhibit a weak shoulder extending between 300 and 400 nm . This is more intense for the dinitro compound indicating that it is a real effect and associated with the 2-nitroaryl chromophore. Thus in both sets of examples the absorption does intrude into the visible region and for this reason all the substituted, nitro ureas are pale yellow. However, the colours are far less intense than for the nitroanilines. Ethyl Centralite on the other hand shows no absorption above 280 nm and is thus white. The spectrum of 2,4'-dinitro ethyl Centralite appears to be simply a combination of the 2,2'- and 4,4'-dinitro isomers and indicates that there is little, if any, communication between the two aromatic rings.

Removal of the acyl group from nitro anilines generally gives rise to peaks at longer wavelength and this is observed in this case. The N-ethyl-2-nitroaniline isomer is an orange oil whilst the 4-nitro analogue is a bright yellow solid and this is a consequence of the longer wavelength of the absorption maximum in the former case. 2,4-Dinitro N-ethylaniline has an absorption maximum shifted more into the ultra violet but is still highly coloured. The absorption maxima and extinction coefficients of the N-ethylanilines closely parallel those of the nitrodiphenylamine analogues(ref.12).

The unsubstituted and 2-nitro nitrosamines are not coloured in their pure form but the 4-nitro isomer, which has slight visible absorption, is a very pale yellow.

5. THIN LAYER CHROMATOGRAPHIC ANALYSIS

Several authors(ref.2,3,13,14) have published thin layer chromatographic data on the ethyl Centralite derivatives though in many cases, the authenticity of the compounds has not been substantiated. Most work has been performed using solvents of 3:1 (v/v) petroleum ether/ethyl acetate and 1,2-dichloroethane. Table 4 summarises the data from present and previous work, and with few exceptions it can be seen that the agreements are very good.

In the present work Merck plastic-backed silica sheets (No 5735), of 0.2 mm silica thickness, were used and heated to 100°C for 15 minutes for conditioning prior to use. Reagent grade 60-80 petroleum ether and ethyl acetate were used. The differences shown in Table 4 are probably due in some part to the type of silica, its water content and differences in the choice of petroleum ether. The use of references is thus strongly recommended rather than purely relying on retention factors based on the solvent front, and this practice has been followed in Table 4.

Ethyl Centralite is a useful reference material to measure the relative retention factors in 3/1 petroleum ether/ethyl acetate and in the present work the absolute value versus the solvent front was 0.56. The urea Centralites are only slowly eluted in 1,2-dichloroethane and N-ethyl-N-nitrosoaniline was more useful as a reference, with a retention factor of 0.66 versus the solvent front. There was no obvious gain in resolution and differentiation in going from a silica to an alumina plate.

As has been noted previously, a single elution in neither of these solvents, nor a 10:9:1 mixture of benzene/dichloromethane/tetrachloromethane(ref.10), was sufficient to separate all the potential derivatives. Rather, two dimensional techniques are better suited. The technique has been used effectively to determine the course of derivatisation in a single and double base propellant and the results indicated that the following derivatives were important. N-ethyl-N-nitroaniline; N-ethyl-2-(and 4)nitro-N-nitrosoaniline; N-ethyl-2-(and 4)nitroaniline; 2,4-dinitro-N-ethylaniline; 2- and 4-nitro ethyl Centralite (unseparated); 2,4'- and 4,4'-dinitro-N-ethyl Centralite. These results were obtained from samples aged at 90°C(ref.2).

An improved method, using a high performance technique has been published recently and the method proposed for use in analysis of propellant and as a replacement for the Abel heat test(ref.14). The key aspect is the monitoring for a new spot which appears in aged samples. This unidentified spot has retention values of 0.38 and 0.64 in 1,2-dichloroethane and 3:1 petroleum ether/ethyl acetate, relative to the solvent fronts. Unfortunately, the values for authentic materials given in reference 14 are somewhat different to those for the other work and correlation is difficult, and no likely candidates emerge for this unknown.

6. THE COLOUR NUMBER

An important and much used method in the analysis of double and triple base propellants is the colour number. This procedure effectively requires the extraction of the coloured derivatives of ethyl Centralite into acetone. Previously, the intensity of the colour was compared with standard samples, but more recently, spectrophotometric analysis has been used(ref.15).

Only three of the derivatives of ethyl Centralite show significant absorption above 400 nm. These are the 2- and 4-nitro-N-ethylanilines and 2,4-dinitro-N-ethylaniline and these compounds are presumably responsible for the origin of the colour number. Some of the other derivatives showed minor absorption in this region but as shown in Table 5 they are not important. Given the similarity of the extinction coefficient of the mononitro-N-ethylanilines at 420 nm then it would appear that this wavelength would be useful for assessing these compounds. In this respect, the result obtained could be expressed as an approximate percentage of nitro-N-ethylaniline. The present spectrophotometric method uses a wavelength of 440 nm for detection which would favour the contributions due to N-ethyl-2-nitroaniline and 2,4-dinitro-N-ethylaniline. This would not be a problem provided that the constancy of the ratio of the two mononitro compounds could be substantiated, but this has not been done.

7. DERIVATIVES OF METHYL CENTRALITE

The methods described in Section 3 are generally applicable to the urea nitro and anilinic derivatives of methyl Centralite. The methyl derivatives are mostly higher melting and less soluble than the equivalent ethyl Centralite compounds. Table 6 shows brief details of these preparations. The list is not complete since the syntheses of some of these complexes were not attempted. The final two entries are for derivatives of N-methyl-4-nitro aniline, a commonly used stabiliser in double-base rocket propellants. Both this stabiliser and its 2-nitro equivalent are commercially available and need not be synthesised although the method described in Section 3.7 is suitable for both of these compounds.

8. ACKNOWLEDGEMENT

The author thanks the Organic Chemistry Department, Adelaide University for use of a nuclear magnetic resonance spectroscopy instrument.

TABLE 1. EXAMPLES OF PROPELLANTS CONTAINING ETHYL CENTRALITE

Type	% Ethyl Centralite	Type	% Ethyl Centralite
AR 5401 (a)	0.6 (d)	BSNACO (a)	1.2
M 7 (b)	0.8	M 8 (b)	0.6
M 9 (b)	0.75	AKB 204 (b)	1.5
MNQF (c)	3.0	MNF 2P (c)	7.5

- a. Single base.
b. Double base.
c. Triple base.
d. Deterrent Coating.

TABLE 2. 80 MHz PROTON NMR SHIFT POSITIONS IN d6-DIMETHYLSULPHOXIDE

	CH ₃	CH ₂	aryl
Ethyl Centralite	1.05	3.38	6.9 to 7.6
2-Nitro Ethyl Centralite	0.94/1.14	3.36/3.72	6.6 to 7.9
4-Nitro Ethyl Centralite	1.03/1.11	3.75	7.0 to 8.3
2,2'-Dinitro Ethyl Centralite	1.09	3.56	6.8 to 7.9
2,4'-Dinitro Ethyl Centralite	0.97/1.22	3.52/3.86	7.0 to 8.2
4,4'-Dinitro Ethyl Centralite	1.16	3.92	7.3 to 8.5
<u>N</u> -Ethyl-2-nitroaniline	1.28	3.50	6.5 to 8.4
<u>N</u> -Ethyl-4-nitroaniline	1.22	3.27	6.6 to 8.3
2,4-Dinitro- <u>N</u> -ethylaniline	1.30	3.59	7.2 to 9.1
<u>N</u> -Ethyl- <u>N</u> -nitrosoaniline	1.07	4.14	6.8 to 8.0
<u>N</u> -Ethyl-2-nitro- <u>N</u> -nitrosoaniline	1.10/1.41	4.14/4.78	7.6 to 8.5
<u>N</u> -Ethyl-4-nitro- <u>N</u> -nitrosoaniline	1.10	4.21	8.0 to 8.7

TABLE 3. ULTRA-VIOLET/VISIBLE SPECTRA

	λ max ($10^{-4}\epsilon$), nm ($\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$)			
	This work	Literature values		
		(ref.12)	(ref.3)	
Ethyl Centralite	247 (0.85)	247 (0.87)	247 (0.87)	
2-Nitro ethyl Centralite	245 (1.29)	245-7 (1.24)	-	
4-Nitro ethyl Centralite	334 (0.81)	334-6 (0.82)	333.5 (0.80)	
2,2'-Dinitro ethyl Centralite	243 (1.64)	-	-	
2,4'-Dinitro ethyl Centralite	241 (1.43)	-	-	
	322 (0.89)	-	-	
4,4'-Dinitro ethyl Centralite	322 (1.52)	323-4 (1.52)	323.5 (1.52)	
N-Ethyl-2-nitroaniline	279 (0.46)	279-80 (0.46)	-	
	425 (0.61)	425 (0.62)	425.5 (0.62)	
N-Ethyl-4-nitroaniline	232 (0.79)	231-2 (0.77)	-	
	386 (1.91)	386 (1.89)	385.5 (1.90)	
2,4-Dinitro-N-ethylaniline	259 (0.90)	259-61 (0.89)	-	
	346 (1.65)	347 (1.66)	347 (1.67)	
<u>N</u> -Ethyl- <u>N</u> -nitrosoaniline	271 (0.69)	270-3 (0.67)	272 (0.66)	
<u>N</u> -Ethyl-2-nitro- <u>N</u> -nitrosoaniline	240 (1.18)	240-2 (1.15)	-	
<u>N</u> -Ethyl-4-nitro- <u>N</u> -nitrosoaniline	313 (1.44)	312-4 (1.50)	313 (1.88)	

TABLE 4. THIN LAYER CHROMATOGRAPHIC DATA

<u>Ethyl Centralites</u>	<u>Solvent A</u>							<u>Solvent B</u>				
	<u>a</u>	<u>b</u>	<u>c</u>	<u>d</u>	<u>e</u>	<u>f</u>	<u>g</u>	<u>a</u>	<u>c</u>	<u>d</u>	<u>f</u>	<u>g</u>
Unsubstituted	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.09	0.12	0.27	0.11	1.00
2-Nitro	0.71	0.67	0.71		0.80	0.74	0.78	0.10	0.16		0.13	0.80
4-Nitro	0.64	0.64	0.63	0.83	0.69	0.63	0.81	0.18	0.29	0.36	0.24	1.32
2,2'-Dinitro	0.48		0.39		0.46	0.30	0.52	0.12	0.27		0.24	0.75
2,4'-Dinitro	0.48	0.42	0.45		0.52	0.45	0.59	0.20	0.37		0.32	1.22
4,4'-Dinitro	0.31	0.24	0.26	0.54	0.38	0.22	0.47	0.25	0.38	0.48	0.34	1.45
<u>N-Ethylanilines</u>												
2-Nitro	1.42	1.48	1.46		1.30	1.45	1.09	1.25	1.41		1.26	1.99
4-Nitro	0.78	0.75	0.82	0.99	0.75	0.80	0.70	0.97	1.02	1.16	0.94	1.72
2,4-Dinitro	0.65	0.64	0.66	0.84	0.69	0.68	0.79	1.10	1.24	1.21	1.20	1.94
<u>N-Ethyl-N-nitrosoanilines</u>												
Unsubstituted	1.48	1.45	1.45	1.19	1.51		1.08	1.00	1.00	1.00	1.00	1.89
2-Nitro	0.55	0.57	0.54	0.60	1.45		0.70	0.93	0.90	0.91	1.26	1.82
4-Nitro	1.05	1.07	1.09	1.00	1.20		0.96	1.05	1.12	1.18	1.10	1.93

Solvent A is 3/1 (v/v) Petroleum ether/ethyl acetate. Solvent B is 1,2-dichloroethane. Retention factors are relative to the internal reference (indicated by a value of 1.00).

- This work (silica)
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TABLE 5. EXTINCTION COEFFICIENTS OF ETHYL CENTRALITE DERIVATIVES, 400-440 nm

	$10^{-4}\epsilon_{400}$	$10^{-4}\epsilon_{420}$	$10^{-4}\epsilon_{440}$
Ethyl Centralite	0	0	0
2-Nitro ethyl Centralite	0	0	0
4-Nitro ethyl Centralite	0.03	0	0
2,2'-Dinitro ethyl Centralite	0	0	0
2,4'-Dinitro ethyl Centralite	0.03	0	0
4,4'-Dinitro ethyl Centralite	0.02	0	0
N-Ethyl-2-nitroaniline	0.48	0.61	0.54
N-Ethyl-4-nitroaniline	1.53	0.65	0.09
2,4-Dinitro-N-ethylaniline	0.63	0.47	0.21
N-Ethyl-N-nitrosoaniline	0.01	0	0
N-Ethyl-2-nitro-N-nitrosoaniline	0.01	0	0
N-Ethyl-4-nitro-N-nitrosoaniline	0.07	0.03	0

TABLE 6. DERIVATIVES OF METHYL CENTRALITE

2-Nitro methyl Centralite ^a	129-30°C (ethanol/petroleum ether)	(ref.7)
4-Nitro methyl Centralite ^{a,b}	144-5°C (acetone/petroleum ether)	(ref.7)
2,2'-Dinitro methyl Centralite	200-1°C (ethanol)	(ref.7)
2,4'-Dinitro methyl Centralite	174-5°C (ethanol)	(ref.7)
4,4'-Dinitro methyl Centralite ^c	156-7°C (4:1 ethanol/acetone)	(ref.7)
2,4-Dinitro- <u>N</u> -methylaniline ^d	179-80°C (1:1 ethanol/acetone)	lit 178°C ^f
<u>N</u> -Methyl-4-nitro-N-nitrosoaniline ^e	98-9°C (ethanol)	-

a. Solid product obtained on addition of reaction mixture to water.

b. Initial purification via column chromatography.

c. Nitration and alkylation routes successful.

d. Aqueous methylamine.

e. Reaction solvent of 3:1 acetic acid/dimethylformamide.

f. "Dictionary of Organic Compounds" J. Buckingham - Editor, Chapman and Hall, New York, 1982 (5th Edition).

REFERENCES

- | No. | Author | Title |
|-----|--|---|
| 1 | Schroeder, W.A.,
Wilson, M.K.,
Green, C.,
Wilcox, P.E.,
Mills, R.S. and
Trueblood, K.N. | Ind.Eng.Chem.,42,539-46, (1950) |
| 2 | Volk, F. | Prop.Explosives,1,90-7, (1976) |
| 3 | Roy, E.J.,
Newbold, B.T. and
MacDonald, R. | "Nitration Reactions of Ethyl
Centralite".
Defence Research Establishment
Valcartier
Report 4013/75 (Canada) |
| 4 | Taymaz, K.,
Newbold, B.T. and
MacDonald, R. | "Nitrosation Reactions of Ethyl
Centralite".
Defence Research Establishment
Valcartier Report 4070/77 (Canada) |
| 5 | Curtis, N.J. | "Methods for the Syntheses of Mono-,
Di-, Tri- and Tetranitro Derivatives of
Diphenylamine".
Defence Science and Technology
Organisation Technical Report,
WSRL-0436-TR (1986) |
| 6 | Mular, M. and
vom Berg, A. | "Preparation of Nitro Compounds VI".
Defence Science and Technology
Organisation Technical Memorandum,
WSRL-0294-TM (1982). |
| 7 | Curtis, N.J. | "N- and O-Alkylations of
1,3-Diphenylureas"
Aust.J.Chem. (In press) |
| 8 | Naegeli, C.,
Tyabji, A. and
Conrad, L. | Helv.Chim.Acta.,1127-43, (1938) |
| 9 | Munch-Petersen, J. | Org.Syntheses,Collected vol 4,715-7 |
| 10 | Wilcox, P.E. and
Schroeder, W.A. | J.Org.Chem.,15,944-9, (1950) |
| 11 | Beaver, D.J.,
Roman, D.P. and
Stoffel, P.J. | J.Org.Chem.,24, 167-6, (1959) |
| 12 | Schroeder, W.A.,
Wilcox, P.E.,
Trueblood, K.N. and
Dekker, A.O . | Anal.Chem.,23,1740-7, (1951) |

No.	Author	Title
13	Yasuda, S.K.	J.Chrom.,16,488-93, (1964)
14	Druet, L., Asselin, M. and Labreche	"High Performance Thin-Layer Chromatography for the Surveillance of Double- and Triple-Base Propellants". Defence Research Establishment Valcartier Report 4418/86 (Canada)
15	Kempson, R.M.	"Colour Testing of Nitrocellulose Propellants by a Spectrophotometric Method". Defence Science and Technology Organisation Technical Memorandum WSRL-0303-TM (1983)

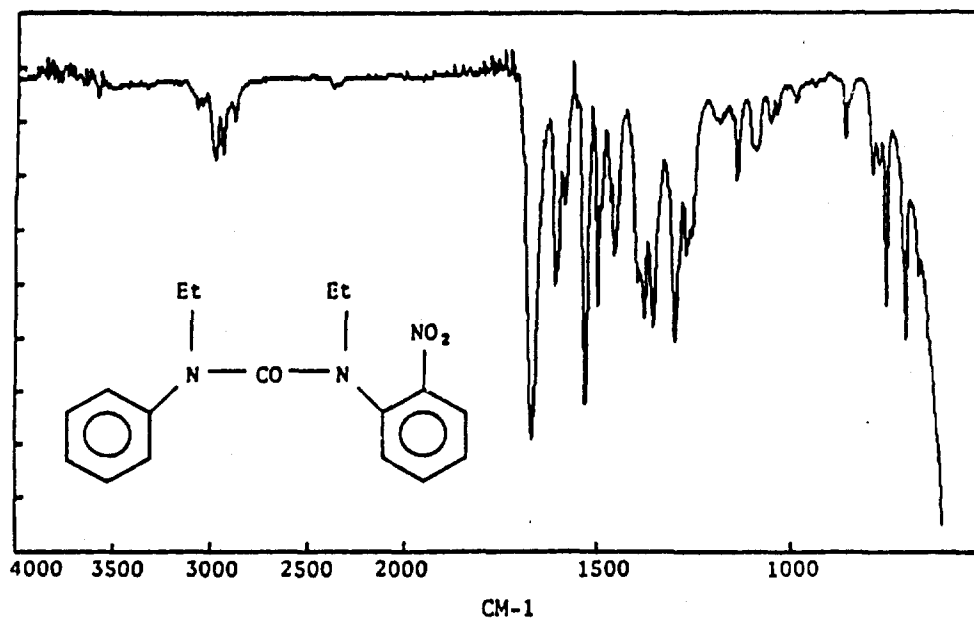
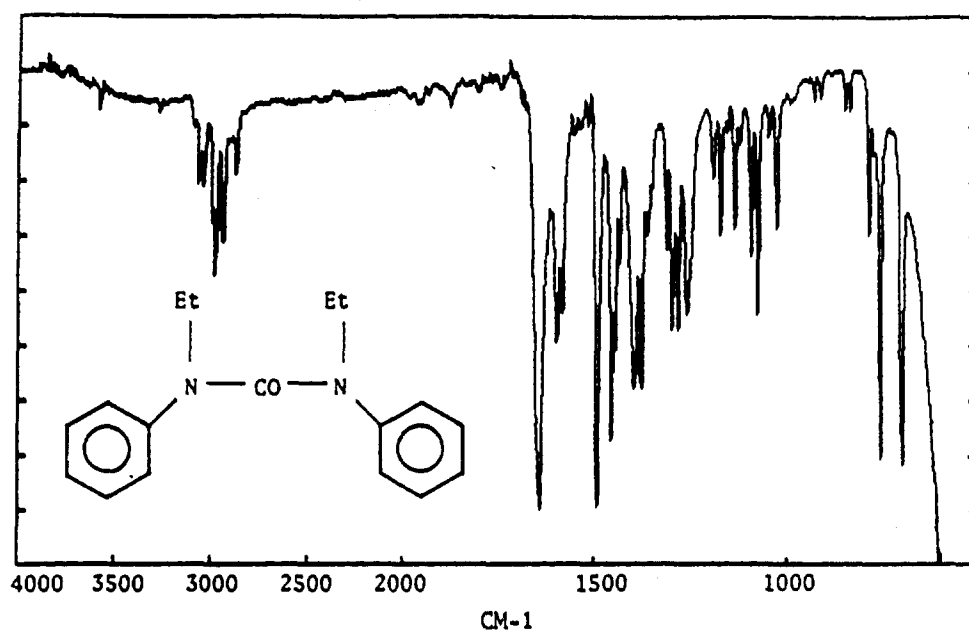


Figure 1. Infra-red Spectra of Ethyl Centralite Derivatives

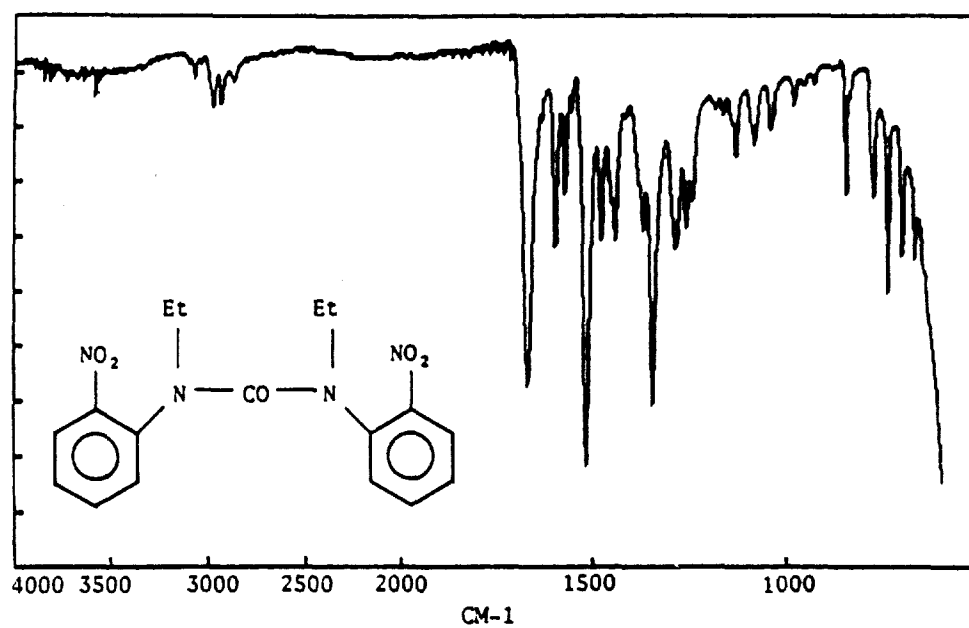
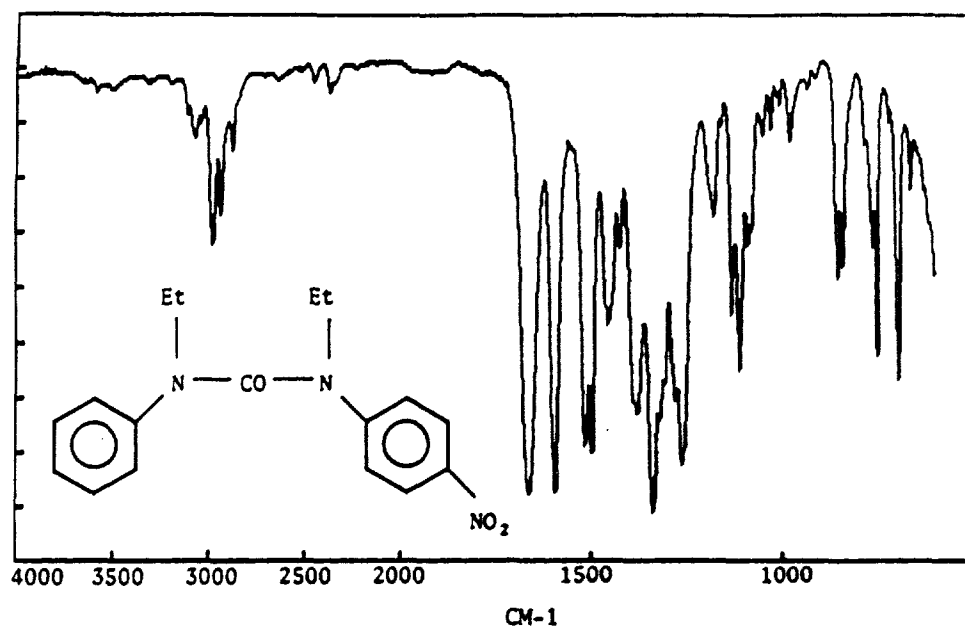


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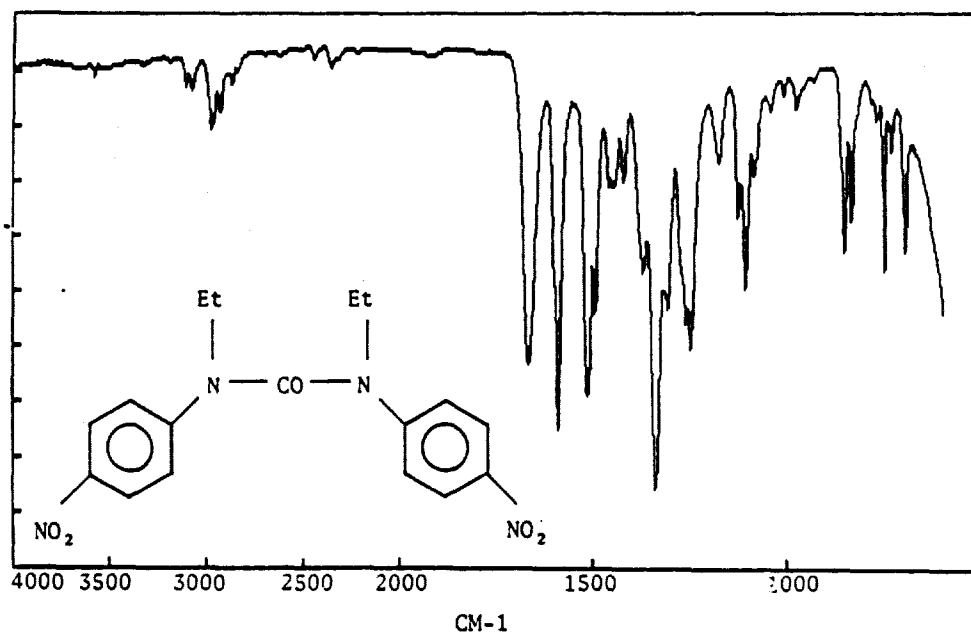
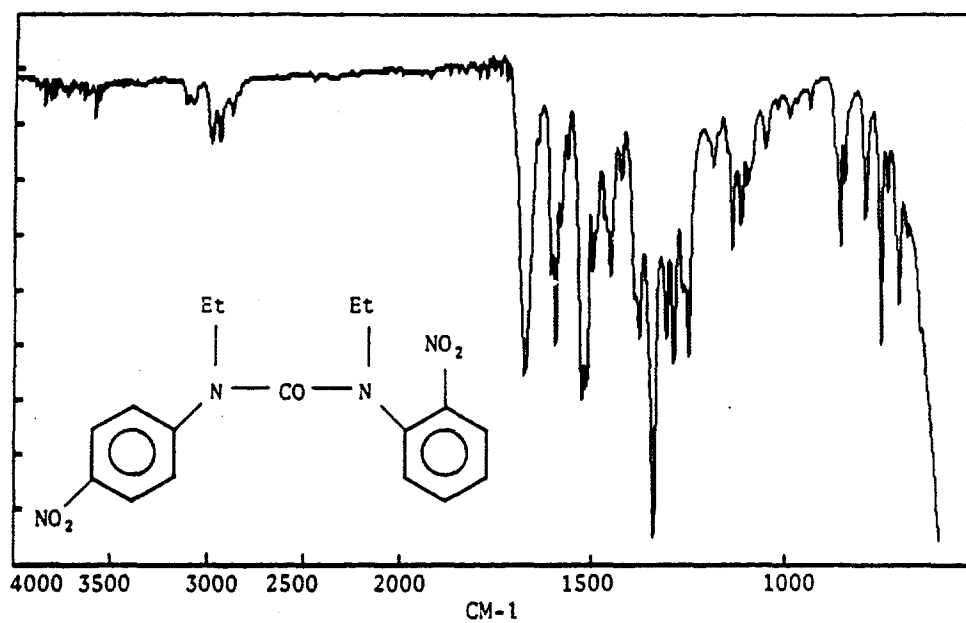


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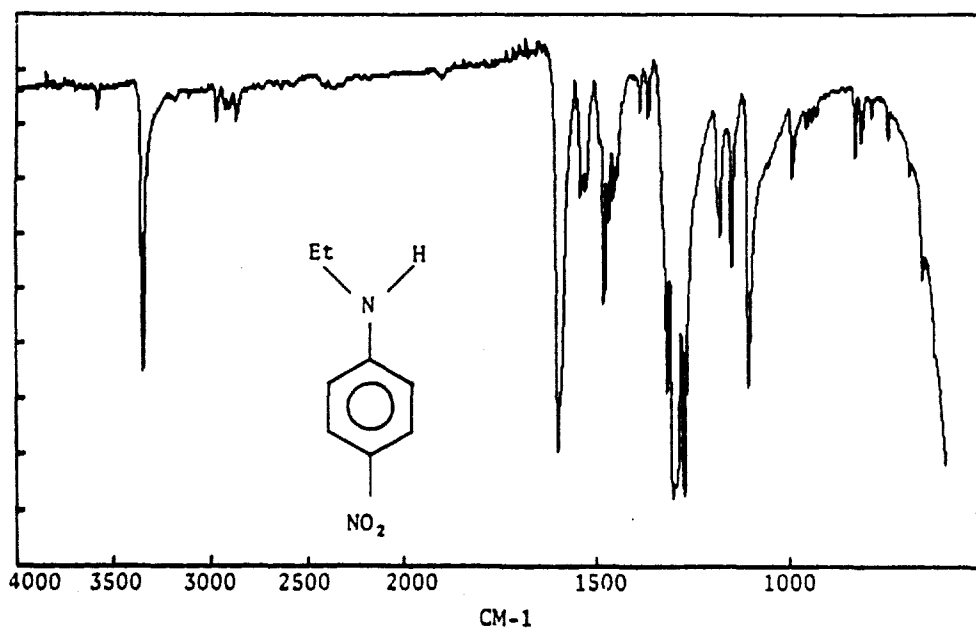
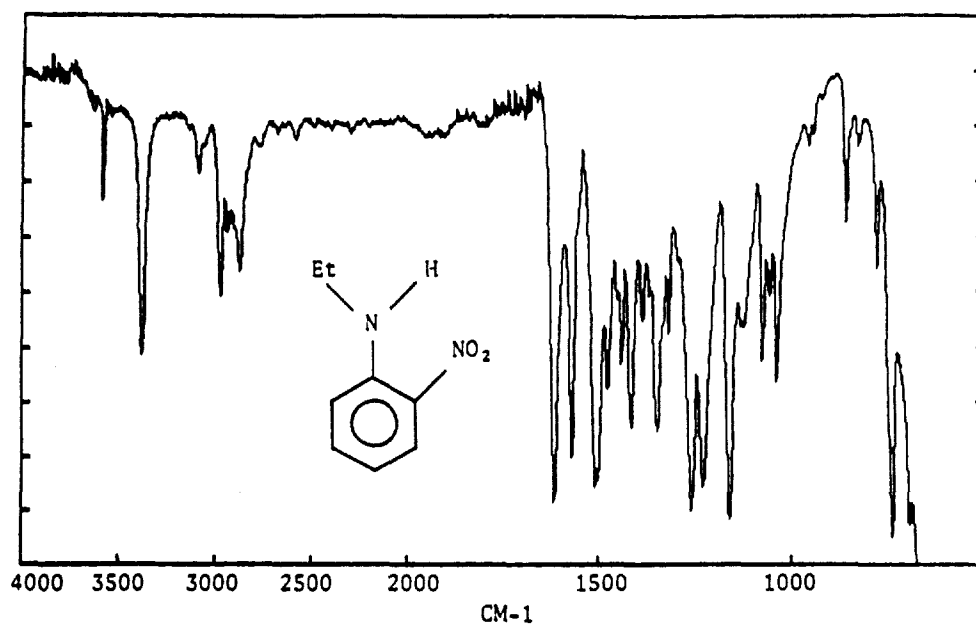


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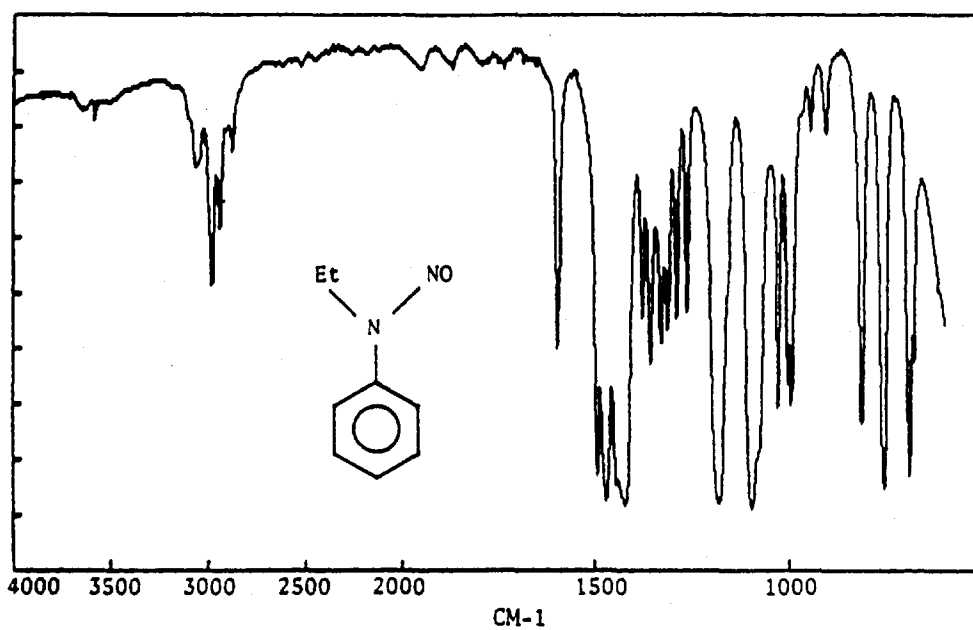
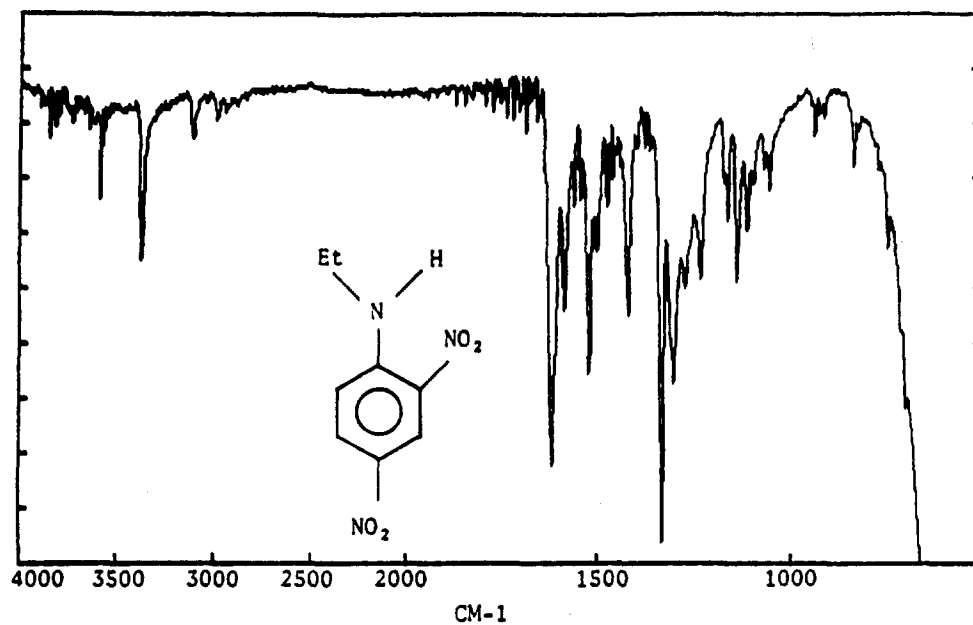


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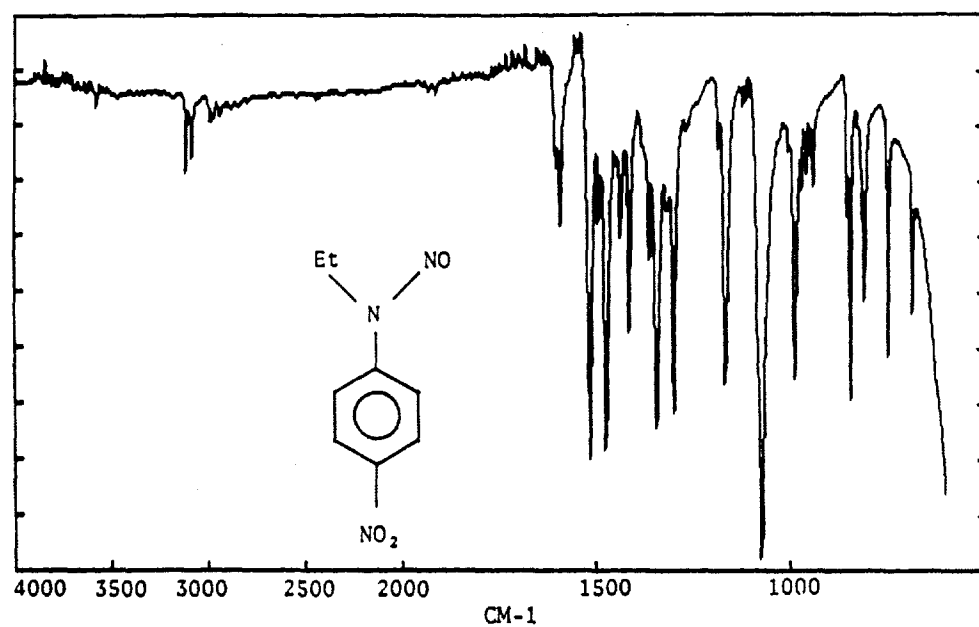
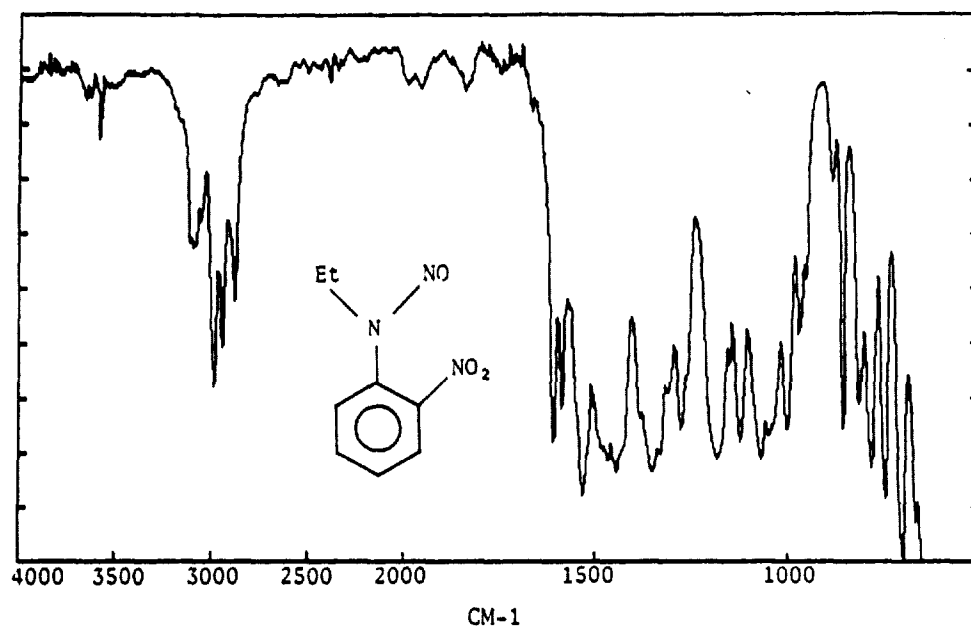


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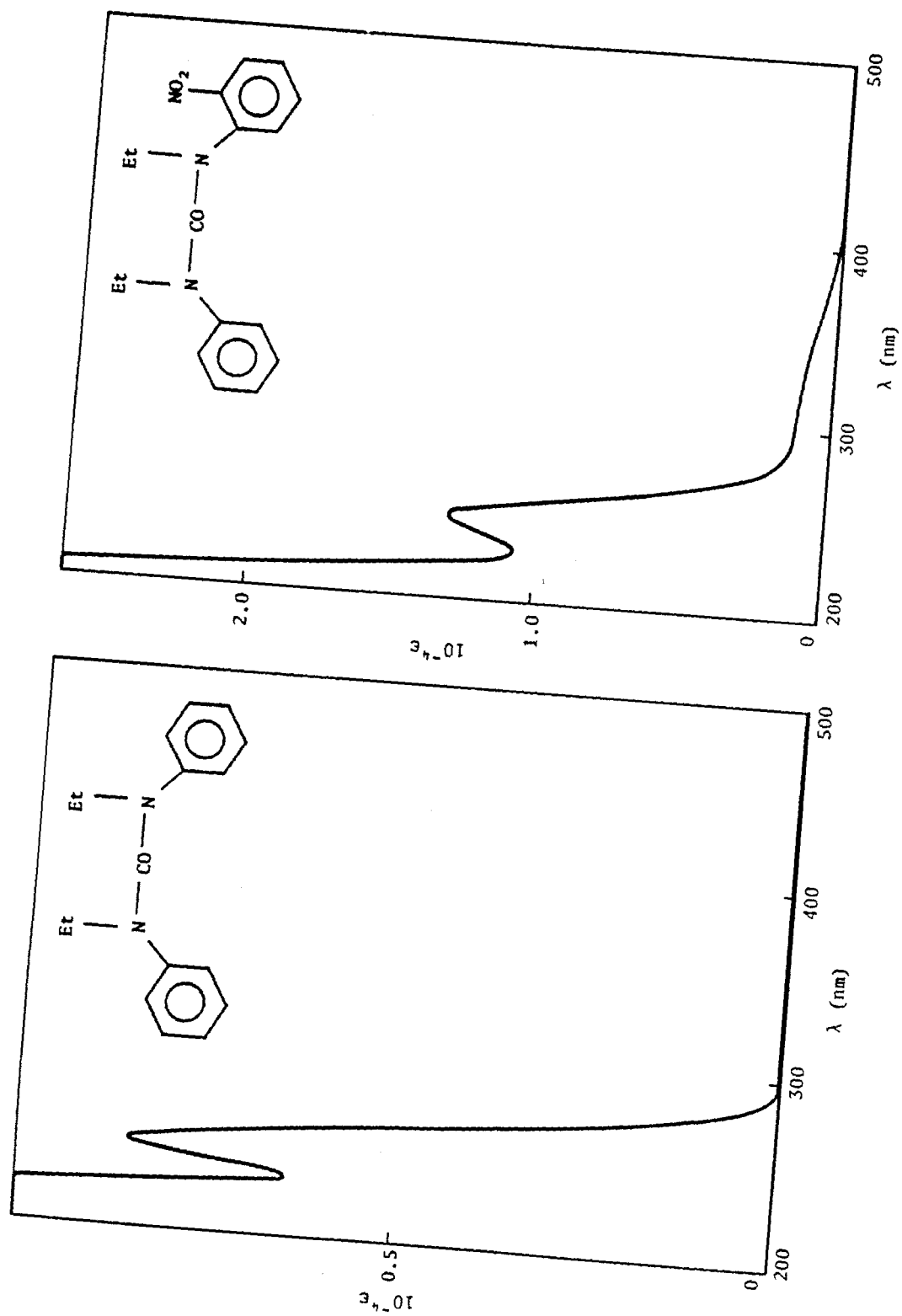


Figure 2. Electronic Spectra of Ethyl Centralite Derivatives

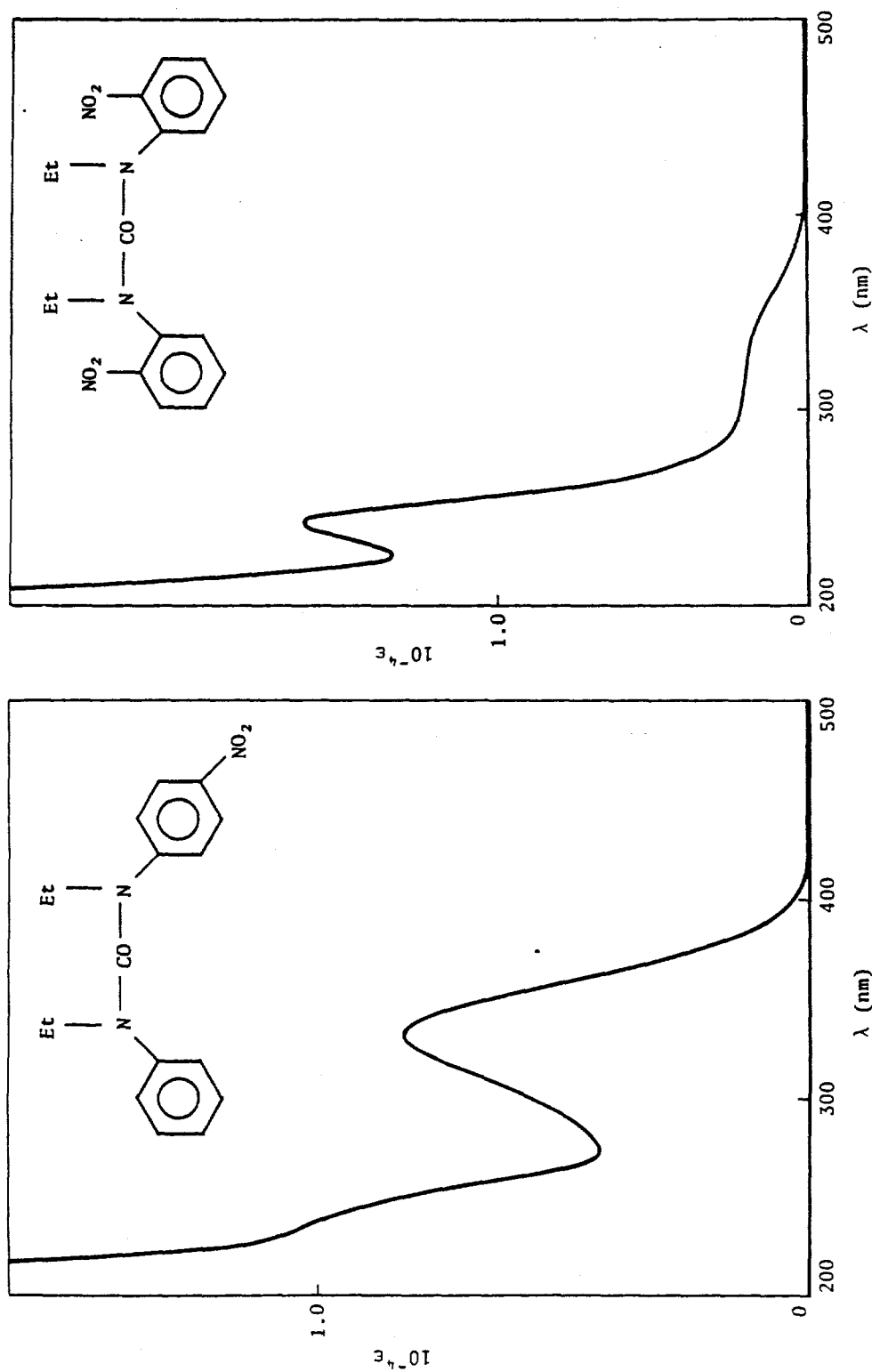


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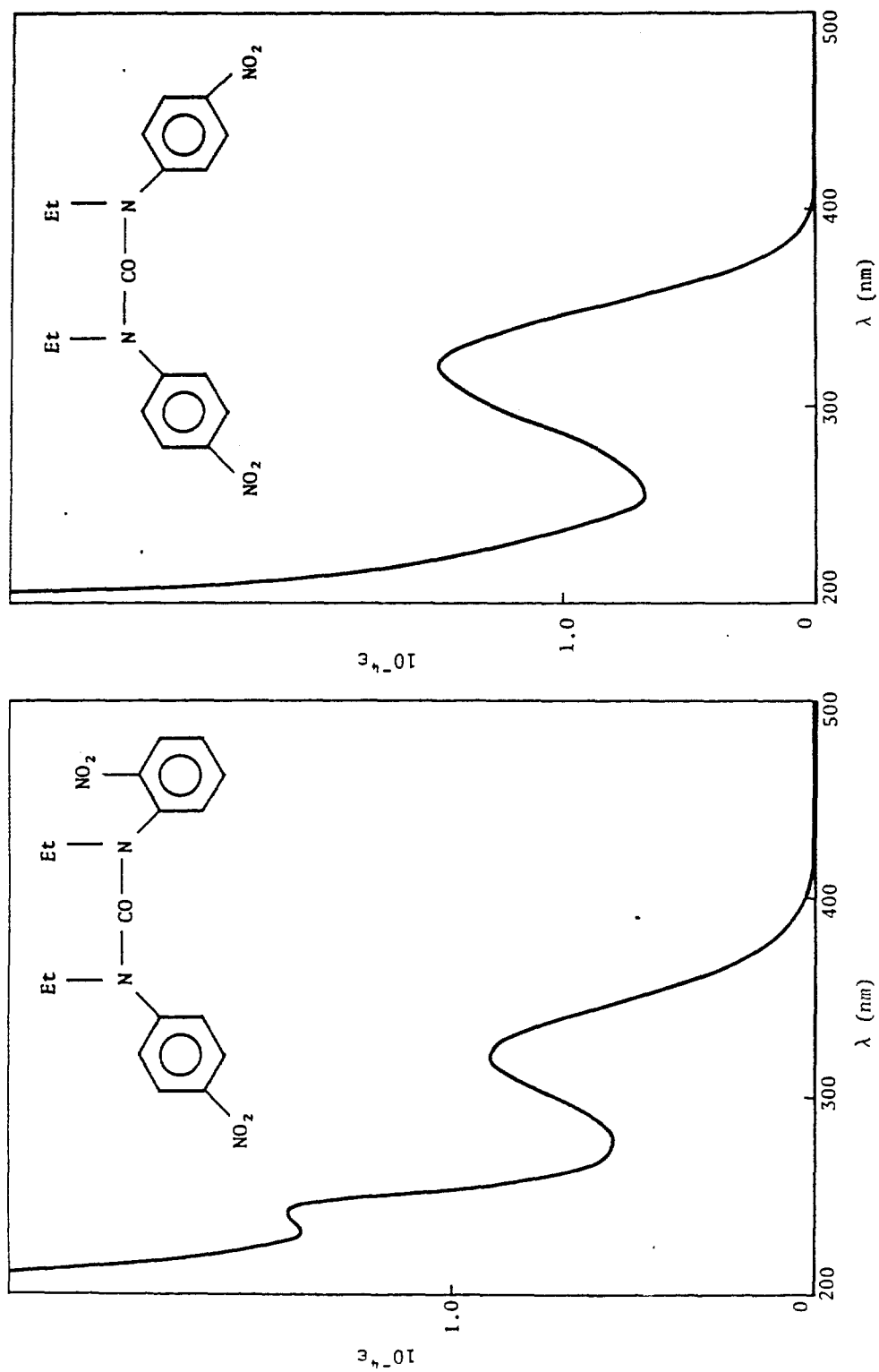


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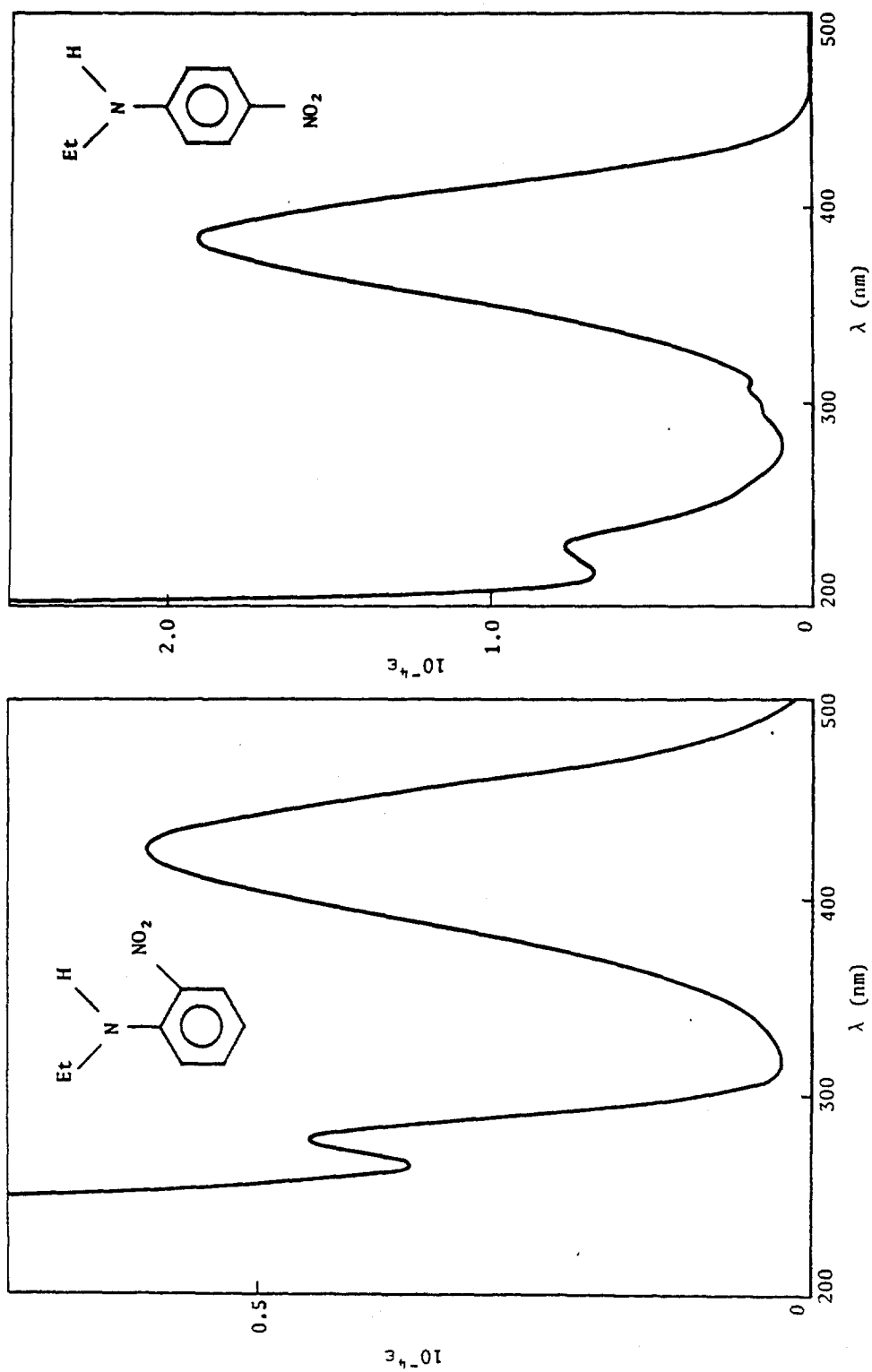


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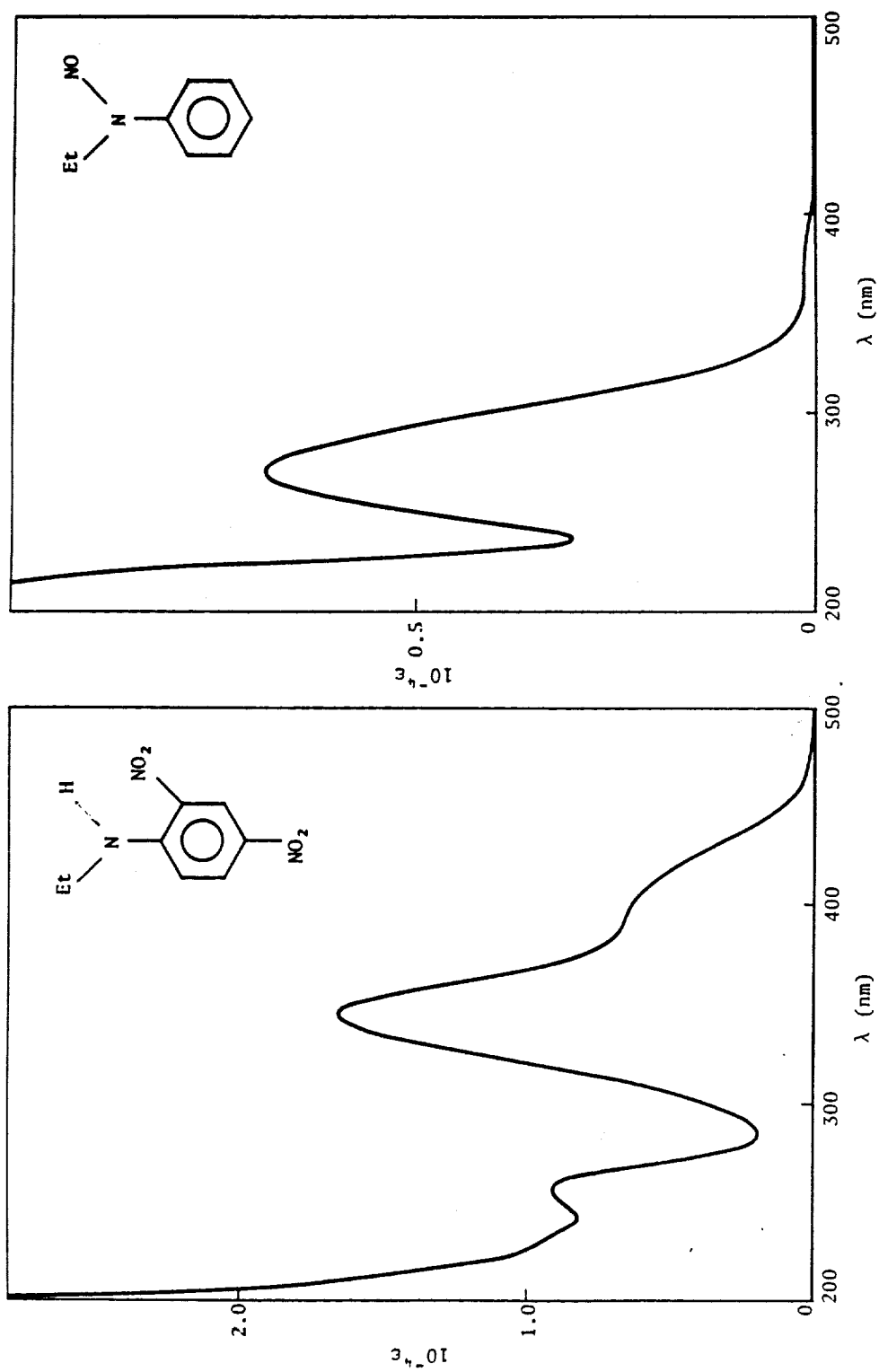


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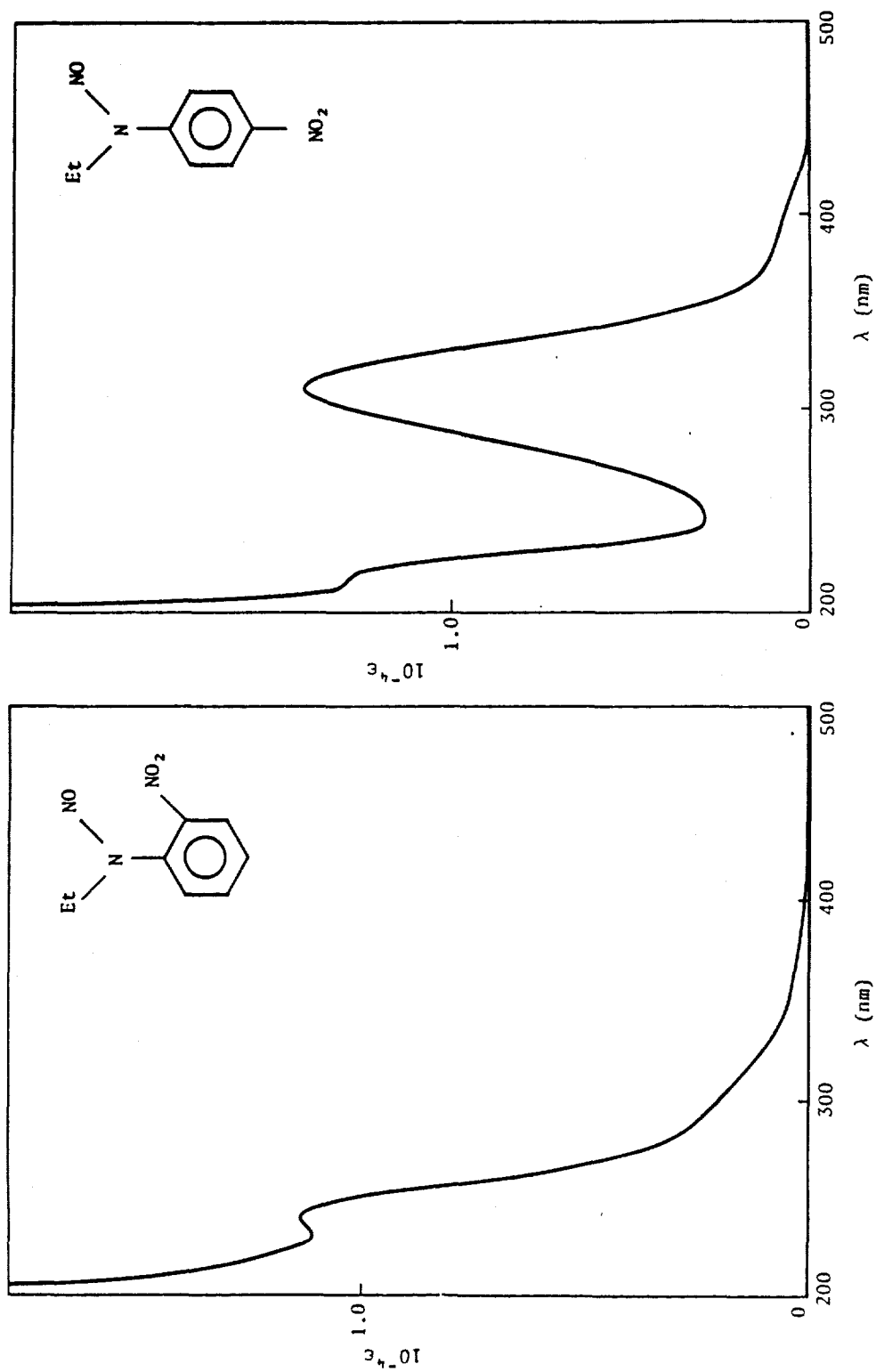


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17 SUMMARY OR ABSTRACT

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A comprehensive description is given of the preparations of all the major derivatives of ethyl Centralites that are found in nitrocellulose based propellants. These compounds are fully characterised by spectroscopic and thin-layer techniques.

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